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Electroluminescence in Mn doped (Zn, Cd)S phosphors

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Abstract : (Zn, Cd)S phosphors with varying concentration of Mn have been synthesised. The voltage dependence of EL-brightness and EL-spectra have been investigated. The EL-spectra are found to show a prominent emission band at about 585 nm which is attributed to $^4T_1 \rightarrow {}^6A_1$ transition of Mn^{2+} ion. The observed concentration quenching and variation of threshold potential have been explained as an effect of efficient resonance energy tansfer among Mn^{2+} ions at higher Mn-concentration. Further, the spectral shift in emission peak and broadening of emission band with Mn-concentration have been explained as due to perturbation of energy levels, pairing and clustering of Mn^{2+} ions.

Keywords : Electroluminescence, EL-spectra, zinc-cadmium sulphide, manganese.

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ZnS and CdS form solid solutions over the whole range of compositions [1] with their band gap lying in visible region and consequently they are finding much significance in the fabrication of opto-electronic devices [2, 3]. The electroluminescence (EL) in (Zn, Cd)S phosphors doped with various activators have been investigated by many workers [4-6]. The behaviour of Mn^{2+} centre in II-VI group compounds has also been studied and reported [7-9]. In this note, the role of Mn^{2+} in (Zn, Cd)S phosphors is reported by investigating the variation of EL-brightness and threshold potential, broadening of 585 nm emission band and spectral shift in peak position of emission band with increasing Mn^{2+} concentration.

(Zn, Cd)S : Mn phosphors were synthesised by heating a mixture of ZnS (60 mole %), CdS (40 mole %) and dopant in the form of soluble salt, at 900°C for one hour in argon atmosphere. The formation of solid solution was confirmed by X-ray diffraction studies. The EL investigations were carried out by forming the usual sandwich type EL-cell [10].

It is evident from Figure 1a that for (Zn, Cd)S : Mn phosphors, the El-brightness shows a power law dependence, $B = AV^n$ over a wide range of applied voltages. The n-value, which is a measure of the rate of change of EL-brightness with voltage, shows a small

unsystematic variation (6.7 to 7.0) with activator concentration. The validity of power law reveals that the EL mechanism is direct field ionization of impurity ion electrons [11, 12].

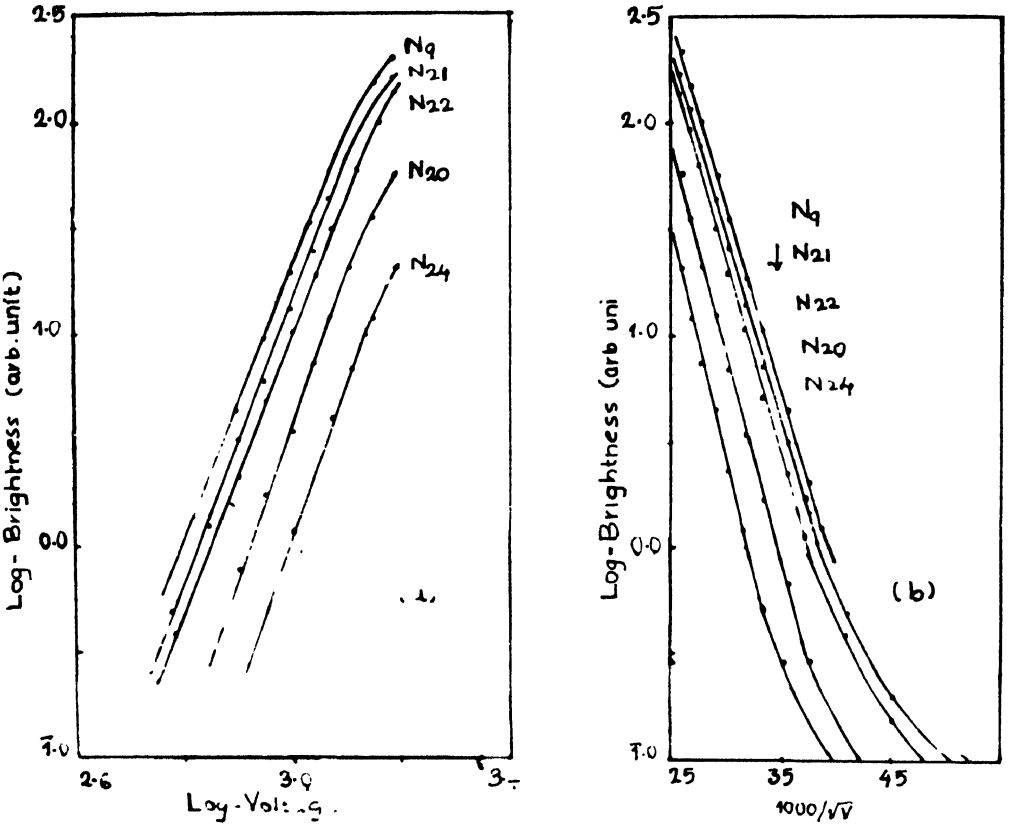

Figure 1. (a) Log $B \rightarrow$ Log V (b) Log $B \rightarrow 1000/\sqrt{V}$. Plot at a.c. exciting frequency of 1 kHz for different Mn-concentrations :

$N_{20} \rightarrow 0.01$; $N_{21} \rightarrow 0.05$; $N_9 \rightarrow 0.1$; $N_{22} \rightarrow 0.5$ and $N_{24} \rightarrow 3.0$ wt % of (Zn, Cd)S.

Besides the power law dependence the EL-brightness follows an exponential relation, $B = B_0 \exp(-b/V^{1/2})$over a limited range of higher voltages (1 kV to 1.5 kV) as depicted in Figure 1b. The exponential relation leads to surmise that Mott-Schottky type exhaustion barriers exist and that the acceleration collision mechanism for EL-emission is favoured at higher voltages [13, 14].

The variation of EL-brightness with Mn concentration (Figure 2a) exhibits concentration quenching with 0.15 wt % as optimum concentration. The initial increase in EL-brightness with Mn-concentration is due to the increase in Mn^{2+} luminescent centres. On the other hand, decrease in EL-brightness at higher concentrations can be explained as an effect of efficient resonance energy transfer among Mn^{2+} ions [15]. The $3d^5$ electrons of Mn^{2+} ion are fully exposed to the interacting fields and hence they interact strongly with each other as well as with crystal field. At higher concentrations the distance between Mn^{2+} ions decreases, as a result they interact strongly with each other and thus increasing the

probability of non-radiative resonance transfer of energy to neighbouring Mn ions. Consequently the excitation moves about several ions before it is emitted as radiation and thereby increasing the probability of losing energy to the quenching traps like Fe^{2+}, Ni^{2+} etc, which are usually present as native impurities in phosphors. The quenching traps (Killer centers) decay by multiphonon emission or by infrared emission. Consequently EL-brightness decreases at higher Mn-concentrations. At optimum concentration (0.15 wt %) the EL-emission process dominates over non-radiative energy transfer to killer centres and eventually gives maximum EL-brightness.

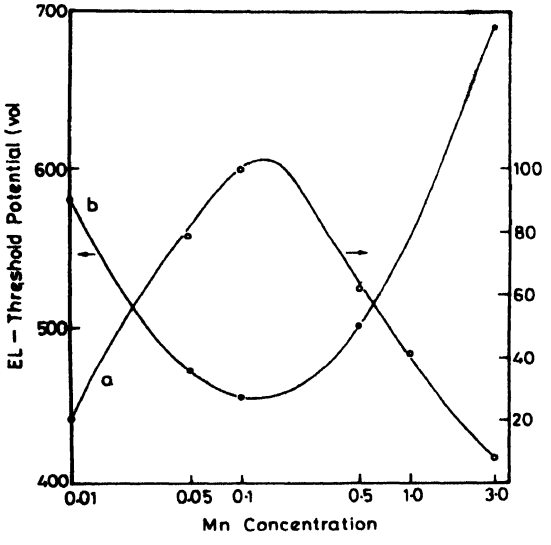

Figure 2. (a) Variation of EL-brightness with Mn-concentration.
(b) Variation of EL-threshold potential with Mn-concentration.

Figure 2b depicts the variation of threshold potential with Mn. The threshold potential is also found to be minimum at the optimum concentration (0.15 wt % of Mn). The variation in threshold potential with activator concentration may also be explained using the concept of resonance energy transfer. With increase in Mn-concentration the population of luminescent centres increases and hence the threshold potential decreases. But at Mn-concentrations greater than optimum (0.15 wt %), the resonance transfer of excitation from Mn^{2+} to killer centres becomes more probable than radiative emission. Consequently more electrical energy is required to induce EL-emission.

Figure 3 shows EL-spectra of the phosphors with different Mn concentration. The spectra show a predominent broad band emission peaking around 585 nm and a very weak side band at about 525 nm. The weak emission at about 525 nm may be an intrinsic defect band arising due to free electron transition from conduction band to deep acceptor level created by zinc vacancy [16]. The characteristic yellow-orange emission may be attributed to the interionic transition $^4T_1 \rightarrow {}^6A_1$ of Mn^{2+} ion [17].

The observed 585 nm emission band exhibits broadening and shift in the peak position towards longer wave length side with Mn concentration. This can be explained as

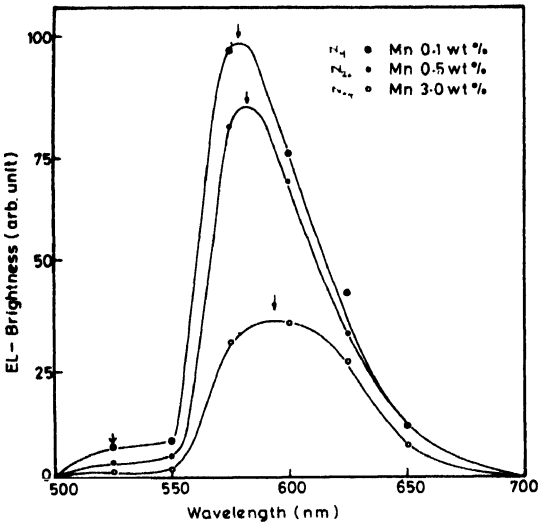

Figure 3. EL-spectra of (Zn, Cd)S:Mn phosphors at various Mn-concentrations (at $f = 1$ kHz and $V = 1.4$ kV)

an effect of perturbation of energy levels of Mn^{2+} ion due to strong interaction with neighbouring Mn^{2+} ions. The ^4G state of Mn^{2+} ion splits in to (^4E, $^4A_1$), $^4T_1$ and $^4T_2$ levels due to perturbing field of surrounding Mn^{2+} ions and crystal field. The $^4T_1$ level shifts to lower energy at stronger interacting ion fields created at higher Mn^{2+} concentration. Eventually emission peak shifts towards longer wavelength side [18]. At higher Mn-concentrations the energy levels do not remain well defined due to perturbation and pairing and clusturing of Mn^{2+} ions as confirmed by electron spin resonance studies [10], consequently the emission bands become still broader.

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